

STATEMENT OF ACCURACY

I, Toshifumi Onuki, c/o TMI ASSOCIATES of 23rd Floor, Roppongi Hills Mori Tower, 6-10-1, Roppongi, Minato-ku, Tokyo 106-6123, Japan, do solemnly and sincerely declare that I well understand the Japanese and English languages and that the attached English version is full, true and faithful translation made by me this 22<sup>nd</sup> day of October 2009 of the granted claims of the Japanese Patent Application No. 2004-194252 filed before the Japanese Patent Office on the 30<sup>th</sup> day of June 2004.

In testimony whereof, I have hereunto set my name and seal this 22<sup>nd</sup> day of October 2009.

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[Claim 1]

A magenta ink composition, wherein when the a\* value in accordance with the CIE standard that is calculated from a visible absorption spectrum is 80 in a 5 diluted aqueous solution with a dilution ratio of 10,000 or less, the b\* value is -29 or less.

[Claim 2]

The magenta ink composition according to claim 1, wherein the L\* value is 60 or less.

10 [Claim 3]

A magenta ink composition, wherein the a\* value in accordance with the CIE standard that is calculated from a visible absorption spectrum is 7 or more in a diluted aqueous solution with a pigment concentration of  $2 \times 10^{-3}$  g/L.

[Claim 4]

15 The magenta ink composition according to any one of claims 1 through 3, comprising C. I. Pigment Violet 32 as the pigment.

[Claim 5]

The magenta ink composition according to claim 4, wherein the concentration of the C. I. Pigment Violet 32 is 4 wt.% or less.

20 [Claim 6]

The magenta ink composition according to any one of claims 1 through 5, comprising a 14-30 wt.% organic solvent with a high boiling point.

[Claim 7]

25 The magenta ink composition according to claim 6, wherein the organic solvent with a high boiling point includes glycerin.

[Claim 8]

The magenta ink composition according to any one of claims 1 through 7, comprising a pigment as a coloring material and also a dispersant for dispersing the pigment at 10-140 wt.% based on the pigment.

5 [Claim 9]

The magenta ink composition according to any one of claims 1 through 8, comprising a 1-20 wt.% permeation enhancer.

[Claim 10]

The magenta ink composition according to any one of claims 1 through 9, 10 comprising 0.01-5 wt.% of at least one of acetylene glycol-type compound and silicone-type compound.

[Claim 11]

An ink cartridge comprising the magenta ink composition according to any one of claims 1 through 10.

15 [Claim 12]

A recording method for forming an image by using the magenta ink composition according to any one of claims 1 through 10.

[Claim 13]

A recording system for forming an image by using the magenta ink 20 composition according to any one of claims 1 through 10.

[Claim 14]

A recorded matter where an image is formed by using the magenta ink composition according to any one of claims 1 through 10.

[Name of Document] Specification  
[Title of the Invention] MAGENTA INK COMPOSITION, INK SET, INK CARTRIDGE, AND RECORDING METHOD, RECORDING SYSTEM, AND RECORDED MATTER USING SAME

5 [Technical Field]

[0001] The present invention relates to a novel magenta ink composition, and more particularly to a magenta ink composition that demonstrates excellent color reproducibility in a high-chroma and low-lightness region and increased luster and suppresses clogging of ink-jet ejection heads.

10 [Background Art]

[0002] An ink using a pigment such as C. I. Pigment Red 202 or C. I. Pigment Red 122 has been suggested as a magenta ink for color ink jet recording (See, for example, Patent Document 1).

[0003] When C. I. Pigment Red 202 and C. I. Pigment Red 122 are used, sufficient color reproducibility in a high-chroma and low-lightness region cannot be obtained unless the concentration of pigments in the ink is comparatively high. However, if the pigment concentration increases, the ink viscosity tends to increase and responsiveness of meniscus tends to become high. For this reason problems are easily associated with the printing speed, quality, and head life. Furthermore, if the pigment concentration is increased, a smooth ink film is difficult to form on a lustrous media and luster of the recorded matter is sometimes degraded.

[0004] A method of decreasing the quantity of glycerin added to the ink is employed to prevent the ink viscosity from increasing.

[Patent Document 1]

25 Japanese Patent Application Laid-open No. 2003-268275

[Disclosure of the Invention]

[Problem to be Solved by the Invention]

[0005] However, because glycerin functions as a wetting agent preventing clogging in ink-jet ejection devices, the ink can easily cause clogging if the content of glycerin is 5 decreased.

[0006] Hence, the object of the invention is to provide a magenta ink that excels in color reproducibility in a high-chroma and low-lightness region, suppresses clogging of ink-jet recording heads, and has increased luster.

[Means for Solving the Problem]

10 [0007] The results of the comprehensive study conducted by the inventors demonstrated that a magenta ink comprising C. I. Pigment Violet 32 as a coloring material has excellent color reproducibility in a high-chroma and low-lightness region even at a comparatively low pigment concentration.

15 [0008] According to an aspect of the invention based on this finding, provided is a magenta ink composition, wherein when the  $a^*$  value in accordance with the CIE standard that is calculated from a visible absorption spectrum is 80 in a diluted aqueous solution with a dilution ratio of 10,000 or less, the  $b^*$  value is -29 or less. It is further preferable that the  $L^*$  value of this magenta ink composition be 60 or less.

20 [0009] Furthermore, the present invention also provides a magenta ink composition in which the  $a^*$  value in accordance with the CIE standard that is calculated from a visible absorption spectrum be 7 or more in a diluted aqueous solution with a pigment concentration of  $2 \times 10^{-3}$  g/L.

25 [0010] All the above-described magenta ink compositions demonstrate excellent color reproducibility in a high-chroma and low-lightness region despite a comparatively low concentration of coloring material. Therefore, the increase in the

ink viscosity caused by the increased concentration of coloring material can be prevented.

[0011] Furthermore, because of the above-described features of the magenta ink composition in accordance with the invention, a wetting agent such as a high-boiling 5 organic solvent with a high viscosity can be added in a sufficient amount. Therefore, even when printing is conducted by using an ink-jet method, the head is prevented from clogging.

[0012] According to another aspect of the invention, provided is a recording method for forming images by using the magenta ink composition. With this 10 recording method, good recorded images with increased luster and excellent color reproducibility in a high-chroma and low-lightness red region can be obtained.

[0013] According to another aspect of the invention, provided is a recording system for forming images by using the magenta ink composition. With this recording system, good recorded images with increased luster and excellent color 15 reproducibility in a high-chroma and low-lightness red region can be obtained.

[0014] According to another aspect of the invention, provided is a recorded matter where images have been formed by using the magenta ink composition. This recorded matter is of high quality, excels in color reproducibility in a high-chroma and low-lightness red region and also has increased luster.

20 [Best Mode for Carrying Out the Invention]

[0015] [Magenta Ink Composition]

The magenta ink composition in accordance with the invention will be described below based on preferred embodiments thereof.

[0016] In the magenta ink composition in accordance with the invention, as 25 described hereinabove, an magenta ink composition is contained in which when the

a\* value in accordance with the CIE standard that is calculated from a visible absorption spectrum is 80 in a diluted aqueous solution with a dilution ratio of 10,000 or less, the b\* value is -29 or less, preferably the b\* value is -35 or less. Such magenta ink excels in color reproducibility in a ultraviolet region, the sRGB color space, which is brightness system coloring, can be color reproduced in a wide range on a recording medium, and the ink can be advantageously used for Desktop Publishing (DTP). On the other hand, if the b\* value becomes -40 or less, the coloring ability of red color deteriorates. For this reason, the b\* value is preferably -40 or more.

10 [0017] Furthermore, in the magenta ink composition in accordance with the invention, in addition to the condition relating to b\* value, it is preferred that the L\* value be 60 or less. With such a structure, color reproduction in a high-chroma and low-lightness region is possible.

[0018] The L\* value, a\* value, and b\* value in accordance with the CIE standard that are calculated from the visible absorption spectrum can be obtained by transmittance measurements carried out by using, e.g., a device U3300 manufactured by Hitachi Ltd. at a scan speed of 600 nm/min, measurement wavelength range 380-800 nm, and slit width 2.0 nm and conducting calculations at a view angle of 2° with a D65 light source (same for other inks).

20 [0019] Furthermore, the magenta ink composition in accordance with the invention has the a\* value in accordance with the CIE standard that is calculated from a visible absorption spectrum of 7 or more in a diluted aqueous solution with a pigment concentration of  $2 \times 10^{-3}$  g/L. In particular, from the standpoint of color reproducibility of a high-chroma region, the a\* value is preferably 8 or more, even more preferably 9 or more. In the magenta ink composition in accordance with the invention, the a\*

value is 7 or more in the case of concentration of  $2 \times 10^{-3}$  g/L, but the a\* value may be 7 or more at other concentrations. The a\* value can be also obtained by a method similar to the above-described measurement method.

[0020] The magenta ink composition in accordance with the invention preferably 5 comprises C. I. Pigment Violet 32 (abbreviated hereinbelow as "PV32") as the pigment. The PV32 can provide sufficient color reproducibility at a comparatively low concentration in a high-chroma and low-lightness region. The concentration of the PV32 is 4 wt.% or less, preferably 2 wt.% or less to prevent the viscosity of the ink from being too high.

10 [0021] The magenta ink of the present invention does not need to contain PV32 when the L\* value is 50 or less and the b\* value is -29 or less given an a\* value of 80 according to the CIE standard as calculated from the visual absorption spectrum using a 10,000 x or lower dilute aqueous solution, or when the a\* value is 7 or more according to the CIE standard as calculated from the visual absorption spectrum using 15 a dilute aqueous solution with a pigment concentration of  $2 \times 10^{-3}$  g/l. For example, C. I. Pigments Red (abbreviated hereinbelow as "PR") 5, 7, 12, 48 (Ca), 48 (Mn), 57 (Ca), 57:1, 112, 122, 123, 168, 184, 202, 207, 209, and C. I. Pigment Violet (abbreviated hereinbelow as "PV") 19 can be contained individually or in combinations of two or more thereof. Those pigments may be also combined with PV32.

20 [0022] The magenta ink in accordance with the invention preferably comprises an organic solvent with a high boiling point in an amount of 14-30 wt.% as a wetting agent. Because the magenta ink in accordance with the invention makes it possible to obtain the target color reproducibility even at a comparatively low pigment concentration, a sufficient amount of organic solvent with a high boiling point can be 25 added without increasing the viscosity. When an organic solvent with a high boiling

point is added in the case of applications for ink jet recording, the ink is prevented from drying and clogging of the ink-jet printer head is inhibited. Examples of organic solvents with a high boiling point include polyhydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, polypropylene glycol, 5 propylene glycol, butylene glycol, 1,2,6-hexane triol, thioglycol, hexylene glycol, glycerin, trimethylolethane, and trimethylolpropane, alkyl ethers of polyhydric alcohols such as ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl 10 ether, and triethylene glycol monobutyl ether, organic alkalis such as urea, 2-pyrrolidone, N-methyl-2-pyrrolidone, 1,3-dimethyl-2-imidazolidinone, and triethanolamine, and saccharides such as sugar alcohol. Those solvents are used individually or in combinations of two or more thereof.

[0023] In particular, in order to prevent clogging and increase luster of the recorded 15 image, it is preferred than the magenta ink composition in accordance with the invention has glycerin added thereto at a ratio of 14 wt.% or more. An organic alkali such as triethanolamine may be added together with glycerin. Triethanolamine also can function as a pH adjusting agent and dispersion stabilizer for the ink and is preferably used within a range of 0.1 to 10 wt.% in the ink.

20 [0024] The magenta ink composition in accordance with the invention preferably uses a pigment as a coloring material and comprises a dispersant for dispersing the pigment. Any dispersant that can be used with the pigment ink of this type can be employed without any limitation. Examples of suitable dispersants include cationic dispersants, anionic dispersant, and nonionic dispersants of surfactants. Examples 25 of anionic dispersants include polyacrylic acid, polymethacrylic acid, acrylic acid –

acrylonitrile copolymer, vinyl acetate – acrylic acid ester copolymer, acrylic acid – acrylic acid alkyl ester copolymer, styrene – acrylic acid copolymer, styrene – methacrylic acid copolymer, styrene – acrylic acid – acrylic acid alkyl ester copolymer, styrene – methacrylic acid – acrylic acid alkyl ester copolymer, styrene –  
5  $\alpha$ -methylstyrene – acrylic acid copolymer, styrene –  $\alpha$ -methylstyrene – acrylic acid – acrylic acid alkyl ester copolymer, styrene – maleic acid copolymer, vinyl naphthalene – maleic acid copolymer, vinyl acetate – ethylene copolymer, vinyl acetate – fatty acid vinyl ethylene copolymer, vinyl acetate – maleic acid ester copolymer, vinyl acetate – crotonic acid copolymer, and vinyl acetate – acrylic acid copolymer. Furthermore,  
10 examples of anionic surfactants include sodium dodecylbenzene sulfonate, sodium laurate, and ammonium salts of polyoxyethylene alkyl ether sulfate, and examples of nonionic surfactants include polyoxyethylene alkyl ether, polyoxyethylene alkyl ester, polyoxyethylene sorbitan fatty acid ester, polyoxyethylene alkyl phenyl ether, polyoxyethylene alkylamine, and polyoxyethylene alkylamide. Those dispersants  
15 can be used individually or in combinations of two or more thereof. From the standpoint of dispersion stability of the pigment, styrene (meth)acrylic acid copolymers are preferred.

[0025] The dispersant is contained in the ink composition usually at 140 wt.% or less, calculated as solids, based on the weight of the pigment.

20 [0026] The dispersant is preferably contained at 10-140 wt.%, even more preferably 10-100 wt.%, and even more preferably 10-40 wt.%, calculated as solids, based on the weight of the pigment. The content ratio of the dispersant in the ink is preferably 0.1-10 wt.%, more preferably 0.3-3 wt.%, calculated as solids.

[0027] Furthermore, from the standpoint of increasing the ability to wet a recording medium and permeation ability of ink, the magenta ink composition in accordance with  
25

the invention preferably contains a permeation enhancer. Examples of permeation enhancers include alcohols such as methanol, ethanol, and iso-propyl alcohol, lower alkyl ethers of polyhydric alcohols such as ethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, triethylene glycol monobutyl ether, propylene glycol monobutyl ether, and dipropylene glycol monobutyl ether, and diols such as 1,2-pentanediol and 1,2-hexanediol. Those enhancers can be used individually or in combinations of two or more thereof. It is preferred that diethylene glycol monobutyl ether, triethylene glycol monobutyl ether, or 1,2-hexanediol, or combinations of two or more thereof be used.

10 [0028] The permeation enhancer is contained in the ink composition at preferably 1 to 20 wt.% or more preferably at 1 to 10 wt.%.

[0029] Furthermore in order to increase the ability of the magenta ink composition in accordance with the invention to wet a recording medium and permeation ability of ink similarly to the permeation enhancer, various surfactants such as anionic surfactants, nonionic surfactants, cationic surfactants, and amphoteric surfactants can be used. It is especially preferred that acetylene glycol compound or silicon compounds be used. Commercially available compounds can be used as the acetylene glycol compounds. Examples of such compounds include Olfine Y and Surfynol 82, 440, 465, 485 (all are the trade names, manufactured by Air Products and Chemicals Co., Ltd.), Olfine STG, Olfine E1010 (both are trade names, manufactured by Nissin Chemical Co., Ltd.). Those compounds can be used individually or in combinations of two or more thereof. It is especially preferred that Olfine E1010 and Surfynol 465 be used. Furthermore, polysiloxane compounds such as BYK347, 348 or BYKUV3510 (manufactured by BYK Chemie Japan Co., Ltd.), which are commercial products, can be used as silicone compounds. The content

ratio of the acetylene glycol compound and/or silicone compound is preferably 0.01-5 wt.%, more preferably 0.1-1.0 wt.%, and even more preferably 0.1-0.5 wt.%.

[0030] In order to shorten the drying time of ink, the magenta ink composition in accordance with the invention can comprise an organic solvent with a low boiling point.

5 Examples of organic solvents with a low boiling point include methanol, ethanol, n-propyl alcohol, iso-propyl alcohol, n-butanol, sec-butanol, tert-butanol, iso-butanol, and n-pentanol. Those solvents can be used individually or in combinations of two or more thereof. Monohydric alcohols are especially preferred.

[0031] The magenta ink composition in accordance with the invention comprises 10 the above-described components, such as pigment, dispersant, organic solvent with a high boiling point, permeation enhancer, acetylene glycol compound, and/or silicon compound and usually contains water as the balance. Pure water or ultrapure water such as ion exchange water, reverse osmosis water, ultra-filtrated water, and distilled water is preferred as the water. In particular, water obtained by sterilizing the 15 above-mentioned water by ultraviolet radiation or addition of hydrogen peroxide is especially preferred because it prevents the appearance of mold or bacteria over a long period.

[0032] If necessary, the magenta ink composition in accordance with the invention can additionally comprise additives such as a fixing agent such as water-soluble rosin, 20 an antiseptic and a bactericidal agent such as sodium benzoate, an antioxidant and a UV absorber such as allophanates, a chelating agent, an oxygen absorber, and a pH adjusting agent. Those additives may be used individually or in combinations of two or more thereof.

[0033] The magenta ink composition in accordance with the invention can be 25 prepared in the same manner as the conventional pigment inks by using the

conventional well-known equipment, for example, a ball mill, a sand mill, an attritor, a basket mill, or a roll mill. In the preparation process, coarse particles can be removed by using a membrane filter or a mesh filter.

[0034] No specific limitation is placed on the application of the magenta ink 5 composition in accordance with the invention, but it is preferably used in an ink-jet recording method, which is a recording method in which fine droplets of an ink are ejected from a nozzle and the droplets are caused to adhere to a recording medium to form the images of letters or figures. It is especially preferred that the magenta ink composition in accordance with the invention be used for on-demand ink-jet recording. 10 Examples of on-demand ink-jet recording methods include a piezoelectric element recording method by which recording is conducted by using piezoelectric elements disposed in a printer head and a thermal heat recording method by which recording is conducted by using thermal energy, e.g., of a heater with a heat-generating resistance element disposed in a printer head. The magenta ink composition in accordance 15 with the invention can be advantageously used in any such ink-jet recording method.

[0035] The magenta ink composition in accordance with the invention can be employed, without limitations, with recording media that are usually used for ink-jet recording methods as a recording media for forming images, and it is preferably employed with the media having a coating layer or the usual paper (recording media 20 in which fibers are exposed on the recording surface). In particular, if the magenta ink composition in accordance with the invention is employed on a media having a coating layer, then a significant suppression of granular appearance caused by dot representation during image formation can be obtained.

[0036] In the present specification, "media having a coating layer" means all the 25 media where the surface (recording surface) where animate is formed by using the

above-described magenta ink composition is covered at least with a coating layer. The media having a coating layer usually has a luster at 85° of 120 or less. Here, the luster at 85° is measured with "PG1M" manufactured by Nippon Denshoku Kogyo K. K. For the measurements, the measurement device is adjusted in advance so as to 5 obtain a 85° luster of a standard luster plate of 100.

[0037] Mirror-finish media with a 85° luster of 70-120, for example, media having a resin coat layer where the contour of an image of a fluorescent lamp can be visually confirmed when the media is illuminated with the fluorescent lamp from a distance of 1 m or more can be used as such media having a coating layer. "PGPP (Premium 10 Glossy Photo Paper) manufactured by Seiko-Epson Co., Ltd. which has a 85° luster of 81 is a representative example of such media.

[0038] Other examples of media having a coating layer include semigloss media with a 85° luster of 10-70 and a matted media with a 85° luster of 10 or less.

#### [Recording Method]

15 The recording method in accordance with the invention will be described below.

[0039] The present invention is a recording method for forming images by using the abovementioned magenta ink composition, that is, a method for forming images by using a magenta ink composition in which when the a\* value in accordance with the 20 CIE standard that is calculated from a visible absorption spectrum is 80 in a diluted aqueous solution with a dilution ratio of 10,000 or less, the L\* value is 50 or less and the b\* value is -29 or less, or a magenta ink composition in which the a\* value in accordance with the CIE standard that is calculated from a visible absorption spectrum is 7 or more in a diluted aqueous solution with a pigment concentration of 2 25 x 10<sup>3</sup> g/L. The recording method employing the abovementioned magenta ink

composition is especially preferred. The recording method in accordance with the invention is implemented similarly to the usual recording method for ink jet recording, except that it uses the above-described magenta ink composition.

[0040] The recording method in accordance with the invention makes it possible to  
5 obtain images with increased color reproducibility in a high-chroma and low-lightness  
red region and luster.

[0041] In the recording method in accordance with the invention, the image is  
preferably formed so that the ink weight at Duty 100% is 7-13 mg/inch<sup>2</sup>.

[0042] Furthermore, in the mixed color, an image is preferably formed so that the  
10 ink weight at Duty 120% is 8-16 mg/inch<sup>2</sup>.

[0043] In the present specification, "Duty" is represented by the unit of D value  
defined and calculated by the following formula.

[0044]  $D = [(number\ of\ actually\ printed\ dots)/(longitudinal\ resolution\ \times\ lateral\ resolution)] \times 100$ . The Duty 100% means the maximum weight of ink of one color  
15 for one pixel.

#### [Recording System]

The invention relates to a recording system for forming images by using the  
above-described magenta ink composition, and a recording system, e.g., a recording  
device such as an ink-jet printer, that uses the magenta ink compositions of the  
20 above-described embodiments is especially preferred.

#### [Recorded Matter]

The invention relates to a recorded matter where images are formed by  
using the above-described magenta ink compositions, and a recorded matter where  
images are formed by using the magenta ink compositions of the above-described  
25 embodiments is especially preferred.

[Modification Examples]

The invention advantageously provides the above-described embodiments, but it is not limited to those embodiments and can be changed in a variety of ways, without departing from the essence thereof.

5 [0045] The invention will be described below in greater detail with reference to the working examples of the invention and test examples, but the invention is not limited by those working examples.

[Working Example]

[0046] [Preparation of Inks]

10 Magenta ink compositions (M1) and (M2) comprising pigment PV32 were prepared as the magenta ink compositions in accordance with the invention.

<Working Example 1 (M1)>

C. I. Pigment Violet 32 4.0 wt.%

Dispersant (styrene – acrylic acid copolymer) 2.0 wt.%

15 Glycerin 14.0 wt.%

1,2-Hexanediol 7.0 wt.%

Triethanolamine 0.9 wt.%

BYK348 0.1 wt.%

Ultrapure water Balance

20 Total 100.0 wt.%

<Working Example 2 (M2)>

C. I. Pigment Violet 32 2.0 wt.%

Dispersant (styrene – acrylic acid copolymer) 1.0 wt.%

Glycerin 20.0 wt.%

25 1,2-Hexanediol 7.0 wt.%

Triethanolamine 0.9 wt.%

BYK348 0.1 wt.%

Ultrapure water Balance

Total 100.0 wt.%

5 Furthermore, a magenta ink composition (m1) containing no PV32 was prepared as a comparative example.

<Comparative Example 1 (m1)>

C. I. Pigment Red 202 2.0 wt.%

Dispersant (styrene – acrylic acid copolymer) 2.8 wt.%

10 Glycerin 12.0 wt.%

1,2-Hexanediol 7.0 wt.%

Triethanolamine 0.9 wt.%

BYK348 0.1 wt.%

Ultrapure water Balance

15 Total 100.0 wt.%

The results obtained in measuring the reverse-flow viscosity are shown in Table 1.

[0047] [Table 1]

	M1	M2	m1	
Reverse-flow viscosity	3.6	3.6	3.6	20

From these results, it appears that although magenta inks M1 and M2 have high glycerin concentrations of 14.0 wt% and 20.0 wt%, respectively, their viscosities are equivalent to that of m1, in which only 12.0 wt% of glycerin is added. This is probably due to the fact that the pigment concentration is relatively low in M1 and M2.

[0048] (Evaluation of Resistance to Clogging)

Resistance to clogging was evaluated for the magenta inks M1 and M2 comprising PV32 (working examples) and magenta ink m1 containing no PV32 (comparative example).

5 [0049] Ink cartridges filled with respective inks were prepared, and heads were filled with the inks by using the ink cartridges in the entire row of unused ink-jet printers PX-G900 (manufactured by Seiko Epson Co.). Then, nozzle check was conducted by using a printer driver to verify whether an abnormality has occurred.

[0050] The ink cartridges were then removed, the heads were removed from the  
10 printers, and the heads were allowed to stay for 10 days in a thermostat at 40°C and a moisture content of 20%. After 10 days, the head and ink cartridges were mounted on the printers and nozzle check was carried out by using the printer driver.

[0051] When an abnormality has occurred, cleaning was conducted by using the printer driver, and nozzle check was then carried out again. When the abnormality  
15 was still detected, cleaning and nozzle check were repeated till the results of the nozzle check indicated a normal state.

[0052] As a result, the heads in which the entire row was filled with the magenta inks M1 or M2 showed a normal output of nozzle check after no more than five cycles of cleaning. On the other hand, the head in which the entire row was filled with the  
20 magenta ink m1 did not show a normal output of nozzle check even after five cycles of cleaning. Those results suggested that the magenta inks M1 or M2 have higher resistance to clogging of the head than the magenta ink m1 of the conventional example and are suitable for an ink jet method. This is apparently because M1 and M2 could contain glycerin, which serves as a wetting agent, at a high concentration  
25 due to a comparatively low pigment concentration.

[0053] (Measurement of L\* value, a\* value, and b\* value of magenta ink in the case of variable Duty)

Inks comprising each of PV32, PV19, and PR202 at 2 wt.%, 4 wt.%, and 6 wt.% were prepared as magenta inks. The ink compositions are presented in Table

5 2.

<PV32: 2 wt.% (Working Example)>

C. I. Pigment Violet 32 2.0 wt.%

Dispersant (styrene – acrylic acid copolymer) 2.0 wt.%

Glycerin 14.0 wt.%

10 1,2-Hexanediol 7.0 wt.%

Triethanolamine 0.9 wt.%

BYK348 0.1 wt.%

Ultrapure water Balance

Total 100.0 wt.%

15 <PV19: 4 wt.% (Comparative Example)>

C. I. Pigment Violet 19 4.0 wt.%

Dispersant (styrene – acrylic acid copolymer) 2.0 wt.%

Glycerin 14.0 wt.%

1,2-Hexanediol 7.0 wt.%

20 Triethanolamine 0.9 wt.%

BYK348 0.1 wt.%

Ultrapure water Balance

Total 100.0 wt.%

<PR202: 6 wt.% (Comparative Example)>

25 C. I. Pigment Red 202 2.0 wt.%

Dispersant (styrene – acrylic acid copolymer) 2.0 wt.%  
 Glycerin 14.0 wt.%  
 1,2-Hexanediol 7.0 wt.%  
 Triethanolamine 0.9 wt.%  
 5 BYK348 0.1 wt.%  
 Ultrapure water Balance  
 Total 100.0 wt.%

Those inks were printed on a medium having a coating layer, and L\* value, a\* value, and b\* value in accordance with the CIE were measured. C\* was then  
 10 found by the following formula by using those values. C\* value was found from  $C^* = (a^{*2} + b^{*2})^{1/2}$ , and h was found from  $h = \tan^{-1}(b^*/a^*)$ .

[0054] More specifically, ink-jet printers PM900 (manufactured by Seiko-Epson Co., Ltd.) were filled with magenta inks, and recorded matters were obtained by printing on the above-described PGPP (manufactured by Seiko-Epson Co., Ltd.) as an example  
 15 of medium having a coating layer. In the course of printing, magenta inks were ejected by changing the Duty from 15% to 255% (ink weight 10-11 mg/inch<sup>2</sup>).

[0055] The L\* value, a\* value, b\* value, C\* value, and h value in accordance with the CIE standard were obtained for the printed products thus obtained by conducting  
 measurements with D50 light source at a view angle 2° by using Macbeth SPM50  
 20 manufactured by Gretag Co., Ltd.

[0056] The measurement results are shown in Tables 2 to 10.

[0057] [Table 2]

PV32\_2%

Duty	L*	a*	b*	C*	h
255	34.26	76.18	5.82	76.4	4.4

230	35.1	77.38	1.17	77.4	0.9
205	36.68	78.58	-6.48	78.8	-4.7
180	38.67	79.05	-14.34	80.3	-10.3
155	43.02	76.88	-20.91	79.7	-15.2
130	50.21	66.96	-23.8	71.1	-19.6
105	59.49	51.22	-22.32	55.9	-23.5
80	69.26	35.53	-18.29	40.0	27.2
55	79.47	20.79	-12.68	24.4	-31.4
30	86.16	11.43	-8.85	14.5	-37.7
15	90.26	5.82	-6.42	8.7	-47.8

[0058] [Table 3]

PV32\_4%

Duty	L*	a*	b*	C*	h
255	30.09	69.36	31.76	76.3	24.6
230	30.67	70.28	28.43	75.8	22.0
205	31.6	71.9	22.37	75.3	17.3
180	32.87	74.09	13.96	75.4	10.7
155	34.68	76.37	3.61	76.5	2.7
130	37.83	76.95	-7.57	77.3	-5.6
105	43.81	71.43	-15.74	73.1	-12.4
80	52.33	59.99	-19.09	63.0	-17.7
55	63.64	43.14	-17.33	46.5	-21.9
30	76.97	23.85	-12.02	26.7	-26.7
15	85.74	11.9	-7.75	14.2	-33.1

[0059] [Table 4]

PV32\_6%

Duty	L*	a*	b*	C*	h
255	26.58	63.58	38	74.1	30.9
230	27.19	64.52	38.45	75.1	30.8
205	28.08	65.94	37.88	76.0	29.9
180	29.4	67.92	33.75	75.3	26.4
155	30.93	70.35	25.07	74.7	19.6
130	33.42	72.83	11.05	73.7	8.6
105	37.76	72.36	-2.49	72.4	-2.0
80	44.94	65.92	-11.88	67.0	-10.2
55	56.99	49.53	-14.87	51.7	-16.7
30	72.56	28.26	-11.75	30.6	-22.6
15	83.39	13.72	-7.87	15.8	-29.8

[0060] [Table 5]

PV19\_2%

Duty	L*	a*	b*	C*	h
255	51.53	80.11	3.25	80.2	2.3
230	52.58	75.59	0.36	79.6	0.3
205	53.77	78.05	-4.68	78.2	-3.4
180	56.72	75.31	-8.28	75.8	-6.3
155	59.29	69.64	-13.29	70.9	-10.8
130	64.61	61.75	-13.33	63.2	-12.2
105	70.09	49.67	-14.48	51.7	-16.3
80	75.25	37.66	-13.8	40.1	-20.1

55	81.36	25.76	-10.79	27.9	-22.7
30	87.2	14.71	-7.68	16.6	-27.6
15	90.7	7.71	-5.81	9.7	-37.0

[0061] [Table 6]

PV19\_4%

Duty	L*	a*	b*	C*	h
255	44.15	79.38	26.25	83.6	18.3
230	44.78	79.83	22.6	83.0	15.8
205	45.84	80.51	16.54	82.2	11.6
180	47.23	80.88	8.75	81.4	6.2
155	49.28	81.07	0.71	81.1	0.5
130	52.35	78.7	-7.1	79.0	-5.2
105	56.72	72.49	-12.48	73.6	-9.8
80	62.55	62.04	-14.79	63.8	-13.4
55	71.1	45.32	-13.92	47.4	-17.1
30	81.07	25.64	-10.81	27.8	-22.9
15	87.56	12.94	-7.36	14.9	-29.6

[0062] [Table 7]

PV19\_6%

Duty	L*	a*	b*	C*	h
255	43.19	76.7	32.28	83.2	22.8
230	43.57	76.85	28.45	81.9	20.3
205	44.59	77.83	22.98	81.2	16.4
180	46.08	79.12	16.17	80.8	11.6

155	48.06	80.06	7.54	80.4	5.4
130	50.82	78.98	-1.21	79.0	-0.9
105	55.18	73.84	-8.4	74.3	-6.5
80	61.31	63.61	-12.39	64.8	-11.0
55	70.1	47.38	-12.57	49.0	-14.9
30	80.32	27.62	-9.7	29.3	-19.4
15	87.15	13.89	-6.82	15.5	-26.2

[0063] [Table 8]

PR202\_2%

Duty	L*	a*	b*	C*	h
255	41.81	81	-16.23	82.6	-11.3
230	42.9	80.07	-18.86	82.3	-13.3
205	44.86	77.58	-22.51	80.8	-16.2
180	47.93	73.33	-25.93	77.8	-19.5
155	52.11	66.15	-28.02	71.8	-23.0
130	57.55	56.34	-28.08	62.9	-26.5
105	63.69	45.19	-26.19	52.2	-30.1
80	70.34	33.13	-23.05	40.4	-34.8
55	77.18	21.78	-17.83	28.1	-39.3
30	84.67	12.2	-11.83	17.0	-44.1
15	89.56	6.13	-7.72	9.9	-51.5

[0064] [Table 9]

PR202\_4%

Duty	L*	a*	b*	C*	h

255	36.25	78.56	5.95	78.8	4.3
230	36.95	79.32	1.98	79.3	1.4
205	38.19	80.18	-4.1	80.3	-2.9
180	40.19	80.82	-11.67	81.7	-8.2
155	43.04	79.31	-18.61	81.5	-13.2
130	47.18	74.34	-24.43	78.3	-18.2
105	52.72	65.11	-26.9	70.4	-22.4
80	59.9	52.12	-26.08	58.3	-26.6
55	69.57	35.63	-21.9	41.8	-31.6
30	80.27	19	-15.24	24.4	-38.7
15	87.3	9.41	-9.63	13.5	-45.7

[0065] [Table 10]

PR202\_6%

Duty	L*	a*	b*	C*	h
255	37.31	79.28	3.18	79.3	2.3
230	38.24	79.6	-2.05	79.6	-1.5
205	40.19	78.89	-9.06	79.4	-6.6
180	43	76.68	-15.48	78.2	-11.4
155	47.36	70.86	-20.49	73.8	-16.1
130	54.29	59.43	-22.42	63.5	-20.7
105	63.09	44.82	-21.27	49.6	-25.4
80	71.92	30.78	-18.15	35.7	-30.5
55	81.03	17.47	-12.56	21.5	-35.7
30	87.18	8.83	-8.45	12.2	-43.7

15	90.93	4.3	-6.04	7.4	-54.6
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FIGS. 1 to 4 show the graphs in which the  $a^*$  values of Tables 2 to 10 are plotted on the abscissa and the  $L^*$  values are plotted on the ordinate.

[0066] FIGS. 1 to 3 show that the magenta ink comprising PV32 has excellent color reproducibility in a region with a high chroma, which is represented by the  $a^*$  value, and a low lightness, which is represented by the  $L^*$  value, at all the concentrations. Furthermore, FIG. 4 demonstrates that the ink comprising PV32, despite a low concentration of 2 wt.%, can provide chroma and lightness identical to those of the ink comprising 6 wt.% of PR202.

(Measurement of  $L^*$ ,  $a^*$ ,  $b^*$  values of diluted aqueous solution of magenta ink)

10 After preparing an aqueous solution containing 4 wt.% pigment of any one type of PV32, PV19, and PR202, the aqueous solution was diluted with water to obtain an  $a^*$  value of 80. The aqueous solution comprising PV32 had to be diluted at a ratio of about 1500, the aqueous solution comprising PV19 had to be diluted at a ratio of about 500, and the aqueous solution comprising PR202 had to be diluted at a 15 ratio of about 660. Table 10 shows the measurement results for the  $L^*$  value and  $b^*$  value in each diluted aqueous solution. The  $L^*$ ,  $a^*$  and  $b^*$  values of each aqueous solution were measured using a Gretag Macbeth SPM50. Specifically, each aqueous solution was loaded into a PM900C (Seiko Epson Co., Ltd.) and printed on the aforementioned PGPP (Seiko Epson Co., Ltd.) as an example of a medium having 20 a coating layer, and the resulting printed matter was measured with a Gretag Macbeth SPM50 with a D50 light source and a view angle of 2 degrees.

[0067] The results are shown in Table 11.

[0068] [Table 11]

	$a^*80$
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	L*	b*	Dilution ratio
PV32_4%	49.51	-38.60	About 1500
PV19_4%	61.04	-16.72	About 500
PR202_4%	50.92	-28.63	About 660

When the a\* value was 80, the L\* value was 50 or less and the b\* value was -29 or less. Excellent color reproducibility in a high-chroma and low-lightness region was obtained only with the aqueous solution comprising PV32.

[0069] Then, aqueous solutions comprising 2% of pigment of one type of PV32, 5 PV19, and PR202 were prepared and diluted at a ratio of 10,000 to obtain aqueous solutions with a pigment concentration of  $2 \times 10^{-3}$  g/L. L\*, a\*, and b\* values were then measured by the above-described methods. The results are shown in Table 12.

[0070] [Table 12]

Dilution ratio	10,000		
	L*	a*	b*
PV32_2%	93.98	9.27	-6.16
PV19_2%	97.50	5.28	-1.86
PR202_2%	97.15	3.41	-2.81

The results obtained demonstrated that of the aqueous solutions with a 10 pigment concentration of  $2 \times 10^{-3}$  g/L, the aqueous solution comprising PV 32 had a\* value of 9 or more and the best color reproducibility in a high-chroma region.

[0071] The above-described results confirmed that the ink set that includes the magenta ink in which when the a\* value in accordance with the CIE standard that is calculated from a visible absorption spectrum is 80 in a diluted aqueous solution with 15 a dilution ratio of 10,000 or less, the L\* value is 50 or less and the b\* value is -29 or less, and the ink set that includes the magenta ink in which the a\* value in accordance

with the CIE standard that is calculated from a visible absorption spectrum is 7 or more in a diluted aqueous solution with a pigment concentration of  $2 \times 10^{-3}$  g/L have excellent color reproducibility in a high-chroma and low-lightness region, are rich in luster, and hardly cause any clogging of ink-jet recording heads.

5 [Brief Description of the Drawings]

[0072] FIG. 1 is a graph illustrating the relationship between  $L^*$  values and  $a^*$  values of magenta inks with pigments of different types.

FIG. 2 is a graph illustrating the relationship between  $L^*$  values and  $a^*$  values of magenta inks with pigments of different types.

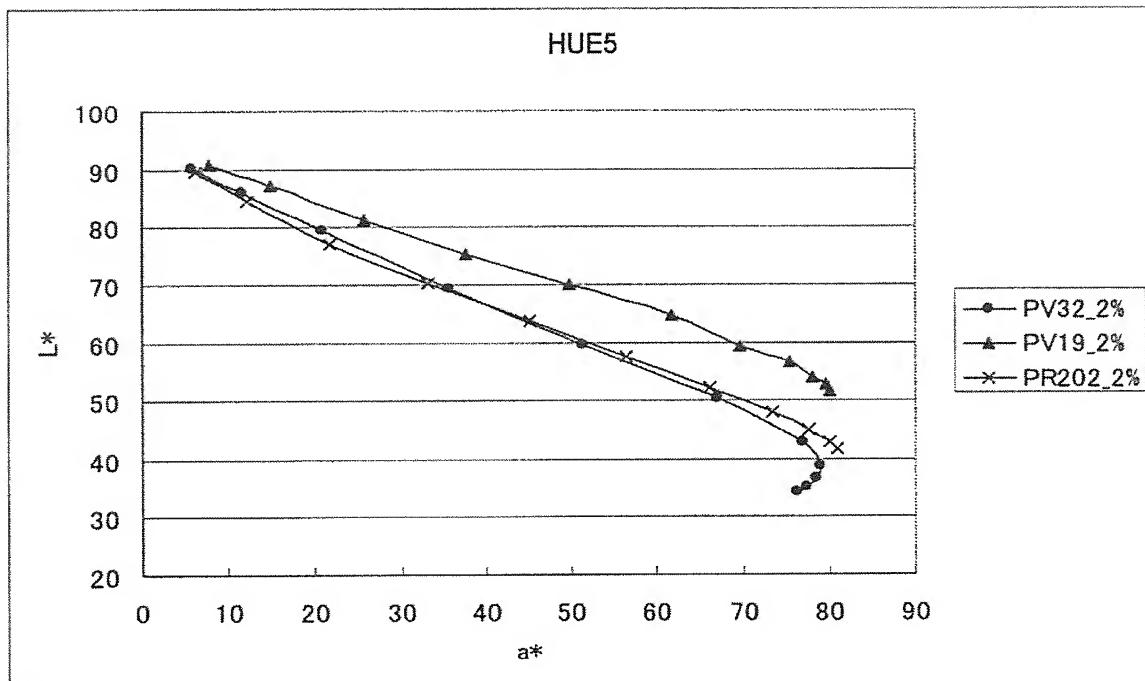
10 FIG. 3 is a graph illustrating the relationship between  $L^*$  values and  $a^*$  values of magenta inks with pigments of different types.

FIG. 4 is a graph illustrating the relationship between  $L^*$  values and  $a^*$  values of magenta inks with pigments of different types.

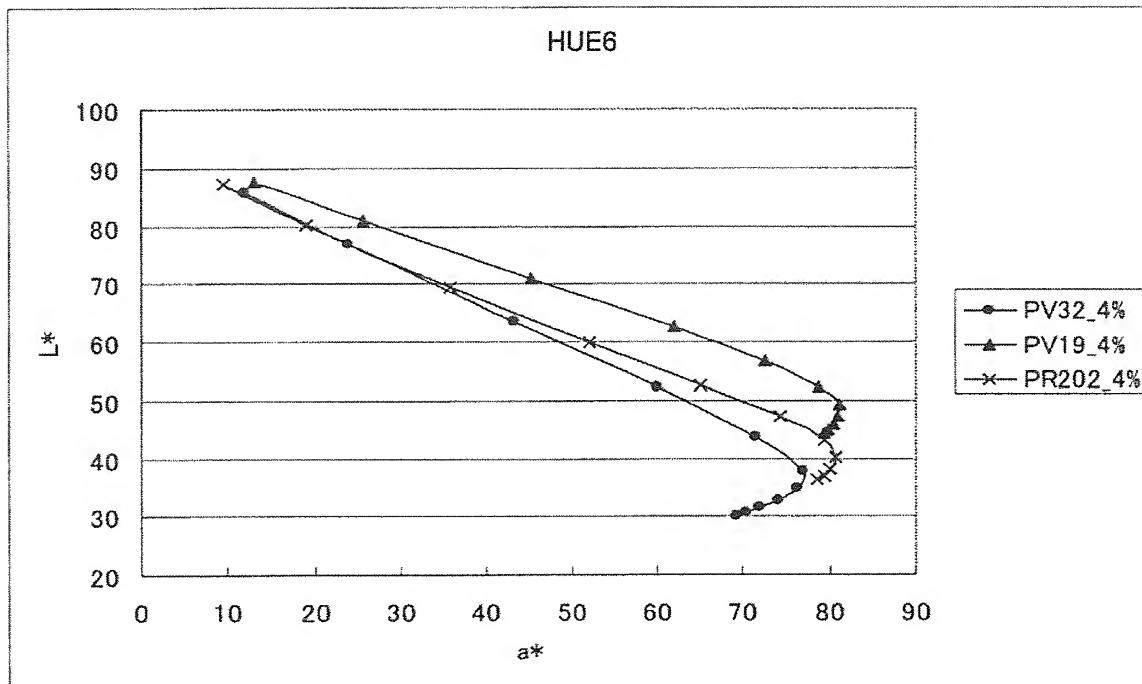
[Name of Document]

Drawings

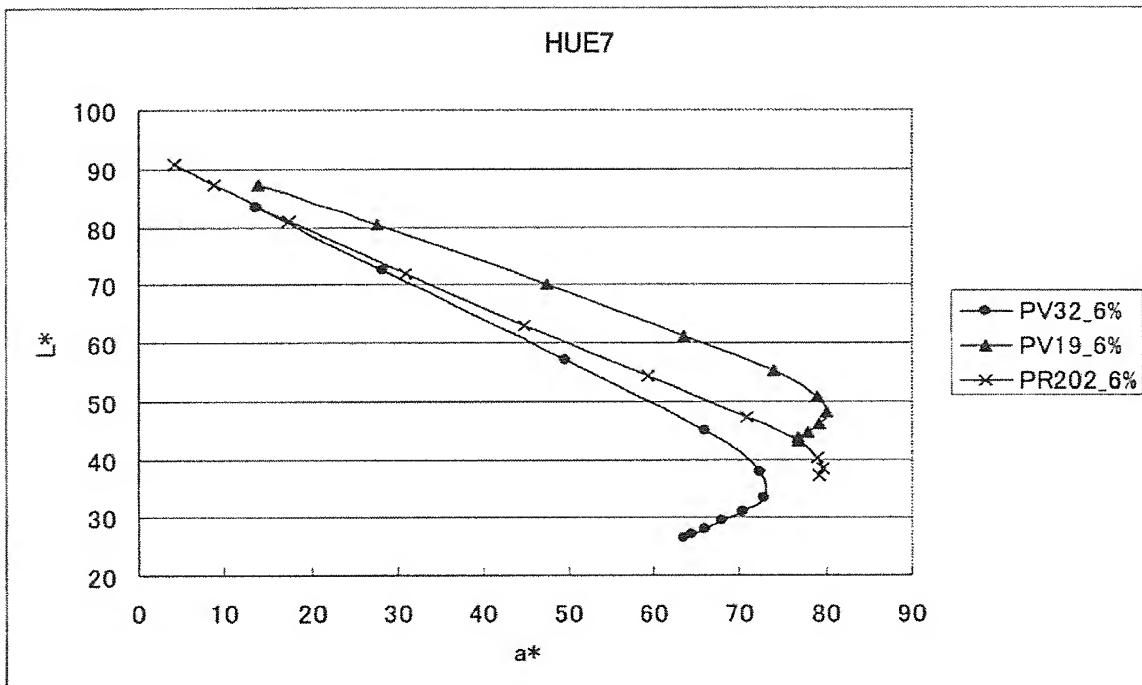
[FIG. 1]



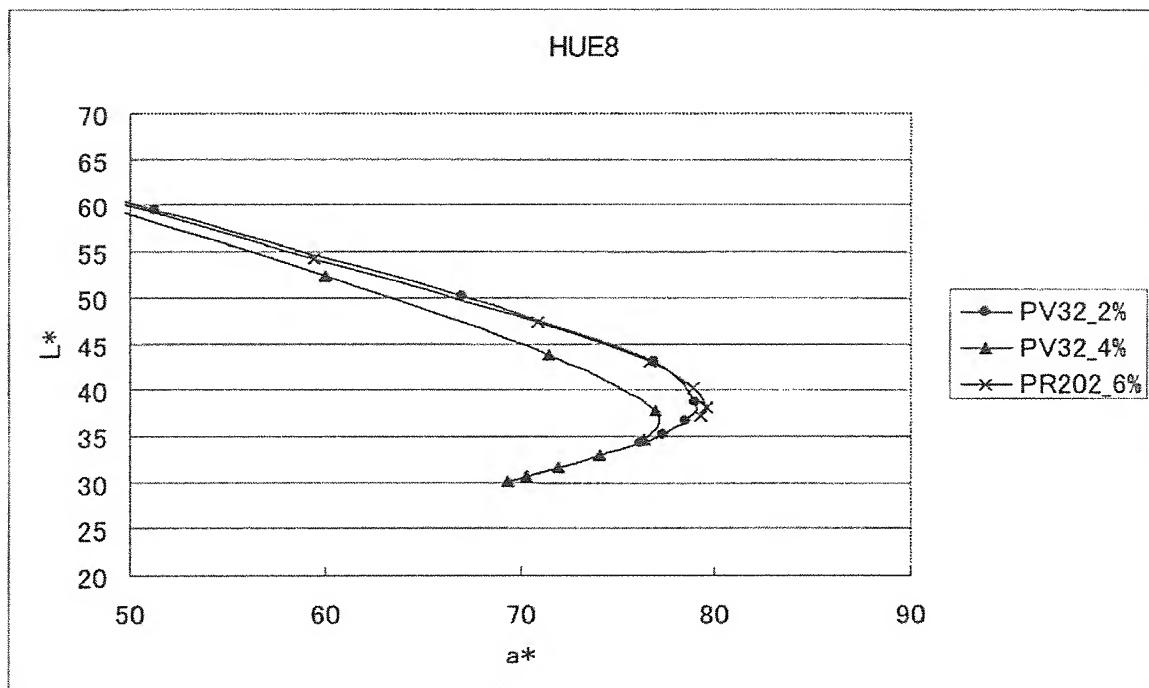
[FIG. 2]



[FIG. 3]



[FIG. 4]



[Name of Document]

Abstract

[Abstract]

[Problem] The object of the present invention is to provide a magenta ink that excels in color reproducibility in a high-chroma and low-lightness region, suppresses 5 clogging of ink-jet recording heads, and has increased.

[Solution] The present invention provides a magenta ink composition, in which when the a\* value in accordance with the CIE standard that is calculated from a visible absorption spectrum is 80 in a diluted aqueous solution with a dilution ratio of 10,000 or less, the b\* value is -29 or less, and the magenta ink composition in which the a\* 10 value in accordance with the CIE standard that is calculated from a visible absorption spectrum is 7 or more in a diluted aqueous solution with a pigment concentration of  $2 \times 10^{-3}$  g/L.

[Selected drawing] None

